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Peculiarities of optical absorption band-edge in irradiated GaP:Te

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The penetrating radiation influence on GaP:Te single crystal characteristics has been studied. It has been shown that the irradiation with 50 MeV electrons results in a gradual degradation of the near-edge absorption due to the non-vertical transitions between the band tails. In samples irradiated with reactor neutrons ($\Phi = 3 \cdot 10^{16}$ cm^{-2}), the crystal parameters are not restored entirely even after radiation defect annealing at 600°C.

Исследовано влияние проникающей радиации на монокристаллы GaP:Te. Показано, что облучение электронами $E = 50$ MeV приводит к последовательной деградации края поглощения за счет невертикальных переходов между хвостами зон. Отжиг радиационных дефектов при 600° С, образцов, облученных нейтронами реактора ($\Phi = 3 \cdot 10^{16}$ cm^{-2}) не приводит к полному восстановлению их параметров.

1. Introduction

The high dose irradiated crystal samples are to be considered as the objects with long-range order lattice disturbances. A disordering level in such systems is as a rule less than those in amorphous substances where the periodicity deviations in the atomic positions appears already within 3 or 4 coordination spheres. The X-ray spectra of semiconductors do not show any essential amorphisation even at $\Phi \approx 10^{18}$ cm^{-2} fluences. But at the same time, their electrophysical and optical constants (the charge carrier concentration and mobility, optical absorption, and luminescence) change appreciably under irradiation. This concerns especially the optical parameters of gallium phosphide [1–6].

The fundamental absorption band edge is known to be highly sensitive characteristics of the perturbation level of the crystal band edges. Its shape and position are the disordering criteria in irradiated samples.

To date, the study of the penetrating radiation effect on the near-edge absorption is far from completion. In the prior works, the destructive influence peculiarities of fast particles on the absorption coefficient in the fundamental transition region were studied [1–6]. In GaP, the edge shape distortion was found to be considerable in comparison with other semiconductors, CdS for example. That may be caused by the active formation of radiation defect-impurity complexes and lattice deformation due to the structure defects in irradiated sample [3]. The point defect accumulation kinetics testifies to the critical role of Te and Zn impurities in complexing. The results obtained in [1–5] are of qualitative character. In [6], data are presented which make it possible to appreciate qualitatively to some extent the radiation defect influence on the appearing of the state density tails.

At the same time, it is to note the absence of literature data concerning the accumulation and annealing kinetics of the disorder region type radiation defects in the crystals irradiated with fast electrons (E_e = 50 MeV) and fast reactor neutrons ($\overline{E}$ = 1 MeV). There is some ambiguity in the annealing mechanism interpretation at its different stages. That is why the aim of this work is to clear the peculiarities of accumulation and annealing of complex defects caused by irradiation with particles inducing the disorder region defects. It is worth to say also that GaP single crystals are used widely in optical instrument industry. The optoelectronic devices operate in penetrating radiation fields of nuclear power plants and in spaceships. Thus, the radiation hardness thereof is under interest, too.

2. Experimental

200–400 μm thick *n*-type GaP samples were grown by Czochralski method and doped with Te at $n = 10^{17}$ cm^{-3} concentration. Te is the main doping impurity in GaP which substitutes phosphorus while being dissolved and thus being a donor. A free carrier concentration rises linearly to $n = 6 \cdot 10^{17}$ cm^{-3} as Te content in the solution increases. The excess tellurium provokes a sublinear dependence because of the second Ga_2Te_3 phase appearing. The Te concentration increases in that case towards the epitaxial film growth [7, 8].

The crystals were irradiated with electrons (E = 50 MeV, $\Phi \approx 10^{17} - 5 \cdot 10^{17}$ cm^{-2}) and fast reactor neutrons ($\overline{E}$ = 1 MeV, $\Phi = 3 \cdot 10^{16}$ cm^{-2}) at room temperature. The isochronous annealing in the 50 to 600°C temperature interval was carried out at 20 min periods of the holding at a constant temperature. The optical absorption was measured at 300 K.

3. Results and discussion

Existence of the state density tails of (SDT) in the initial highly doped and compensated semiconductors causes an exponential increase of the absorption coefficient $\alpha(\hbar\omega = h\nu)$ in the near-edge region according to the Urbach law [9]

$$\alpha(\omega) \sim \exp\left(-\frac{\hbar(\omega_0 - \omega)}{\Delta}\right), \quad \Delta = cT,\ c = const, \tag{1}$$

where Δ is the characteristic energy.

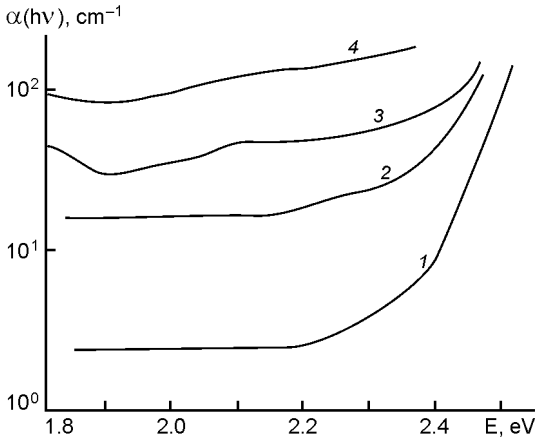

Fig. 1. Dependences of the absorption coefficient $\alpha(h\nu)$ of *n*-type GaP irradiated with 50 MeV electrons at fluence Φ, cm^{-2}: 0 (*1*); $3 \cdot 10^{16}$ (*2*); 10^{17} (*3*); $5 \cdot 10^{17}$ (*4*).

The experimental dependences of the absorption coefficient $\alpha(h\nu)$ in the fundamental transition region for initial and irradiated with 50 MeV electrons *n*-type GaP are shown in Fig. 1. It is seen that the exponential $\alpha(h\nu)$ increase occurs in the interval $h\nu$ = 2.2–2.5 eV for the initial sample. The Urbach law is valid for 2.4–2.5 eV region and also valid in part in the $h\nu$ = 2.3–2.4 eV region for the sample irradiated at $\Phi = 3 \cdot 10^{16}$ cm^{-2} (E_e = 50 MeV), but the characteristic energy is higher in this case ($\Delta_{init.}$ = 0.053 eV, $\Delta_{irrad.}$ = 0.081 eV). The characteristic energy parameter Δ is known to be the crystal defect measure, which provides an estimation of the structure defect concentration that influences the optical absorption [10]:

$$\Delta = 2.2(n_t a_B^3)^{2/5} E_b, \tag{2}$$

$$n_t = \left(\frac{\Delta}{2.2E_B}\right)^{5/2} \frac{1}{a_B^3}, \tag{3}$$

where n_t is the defect concentration; a_B, the Bohr radius of electron in the crystal

$$a_B = \frac{\varepsilon\hbar^2}{me^2}, \tag{4}$$

which differs from the Bohr radius of isolated hydrogen atom by the dielectric permittivity ε of material

$$E_B = \frac{m^* e^4}{2\varepsilon^2\hbar^2} \tag{5}$$

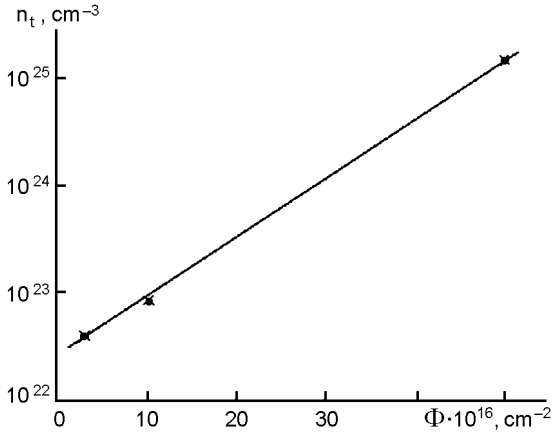

Fig. 2. Concentration of optically-active centers as the dose function for n-type GaP irradiated by 50 MeV electrons.

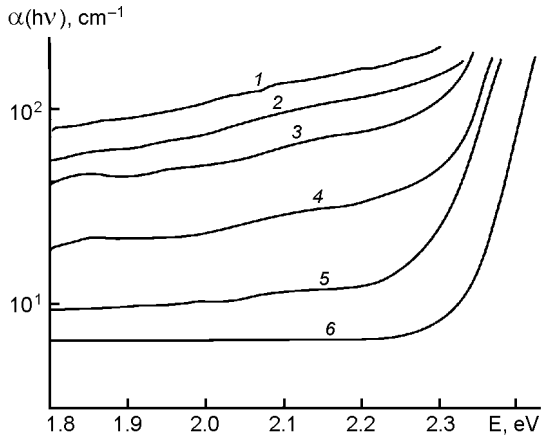

Fig. 3. Restoring of the absorption coefficient $\alpha(h\nu)$ of neutron-irradiated GaP sample in the course of isochronous annealing: as-irradiated (*1*); annealed at 200°C (*2*); 300°C (*3*); 500°C (*4*); 600°C (*5*); initial (*6*).

is the Bohr energy E_B in the crystal expressed by the carrier effective mass m^* and thus being a constant only for the specific crystal lattice.

The n_t estimation results for irradiated GaP ($\varepsilon_{GaP} = 11$, $m_e^* = 0.1$ m) are given in Fig. 2 as the concentration optically active centers as a function of dose. This defect concentration is obviously overestimated, however, the curve in Fig. 2 reflects objectively the defect accumulation kinetics during irradiation. The nonlinearity of $n_t(\Phi)$ may result from formation of defect clusters, which geterate considerable inner fields. According to the Franz-Keldysh effect, those fields decrease the barrier height down to

$$d' = \frac{E_g - h\nu}{q_0 \varepsilon}, \qquad (6)$$

where q_0 is the electron charge; ε, the electric field intensity) and increase the probability of tunnel transition involving a photon. The absorption edge must shift towards a lower energy. It is seen in Fig. 1 for $\alpha(h\nu)$ of a sample irradiated with an intermediate electron fluence $\Phi = 3 \cdot 10^{16}$ cm^{-2}. The further increase of the integral electron fluence results in a gradual distortion of the absorption edge due to non-vertical transitions between the band tails which may reach the middle of the forbidden ban at $\Phi \geq 5 \cdot 10^{17}$ cm^{-2}. It is to note that if the crystal includes the large-scale defect accumulations, the scattering of light quanta increases, thus contributing additionally to the measured absorption coefficient.

The formation of disorder regions during neutron irradiation is known [6]. It is of interest to study their thermal stability in GaP. An isochronous annealing of neutron-induced radiation defects ($\Phi = 3 \cdot 10^{16}$ n/cm^2) was carried out in 300–600 K temperature interval. The $\alpha(h\nu)$ dependences for initial sample and those annealed at different temperatures are shown in Fig. 3. It is obvious that an essential part of non-annealed defects still exists in a sample after $T_{ann} = 600$°C. However, a further heating of the crystal is not desirable due to the formation of thermal defects which deteriorate sharply the crystal uniformity [11]. The Urbach law is valid for the initial sample heated at 600°C in the 2.3–2.4 eV region.

Concentration of defects n_t which influence on absorption according the equation (3) depends exponentially on the annealing temperature (Fig. 4). The diffusion equation (second Fick's law) in the case when the diffusing component concentration C is equal to the sample defect concentration n_t can be written as

$$D\nabla^2 n_t = \frac{\partial n_t}{\partial t}. \qquad (7)$$

The diffusion coefficient $D = \gamma a^2 \nu$ is defined by the lattice constant a; γ is a numerical coefficient depending on the lattice geometry and position of neighboring defects; ν, the frequency of defect jumping

which, according to the Arrhenius expression, is

$$\nu = \nu_0 e^{-\frac{E_A}{kT}}, \quad (8)$$

where $\nu_0 = 10^{13}$ s^{-1} is the vibration frequency of penetrating atoms. Thus, the temperature dependence of D is exponential with activation energy E_A.

Let drain regions of radiation defects to exist in the sample with absorbing surfaces where $n_t = 0$. Then series of functions can be written for a separate region for which

$$\nabla^2\varphi_i(r) + \lambda_i\varphi_i(r) = 0 \quad (9)$$

over the whole region. At the boundaries, $\varphi_i = 0$. λ_i are constants defined by the shape and dimension of the region and $\lambda_0 < \lambda_1 < \lambda_2$. The $\varphi_i(r)$ functions are orthogonal. The solution of the previous equation for φ_i is a sum [12]

$$C(r,t) = \sum_{i=0}^{\infty} a_i\varphi_i(r)e^{-\lambda_i Dt}. \quad (10)$$

Substituting one of the items into the differential equation for $\varphi_i(r)$, an identity is obtained.

It is clear from the solution that the defect concentration in every point r decreases as the sum of the exponentially dropping functions. At long observation time t, the high order terms with larger λ can be assumed to disappear more rapidly. Therefore,

$$C(r,t) \cong a_0\varphi_0 e^{-\lambda_0 Dt}. \quad (11)$$

This equation describes the first order reaction where

$$\frac{dn_t}{dt} = -kn_t; \quad k = \lambda_0 D. \quad (12)$$

In general, the concentration change rate is

$$\frac{dn_t}{dt} = -K_0\exp\left(-\frac{E_A}{kT}\right)f(n_t), \quad (13)$$

where K_0 is a constant; $f(n_t)$, a function which defines the reaction order between the defects.

At isochronous annealing, the temperature is linear time function $T = at + T_0$; $dT = adt$, then

$$\frac{d(n_t)}{dT} = const_1\exp\left(-\frac{E_A}{kT}\right)f(n_t). \quad (14)$$

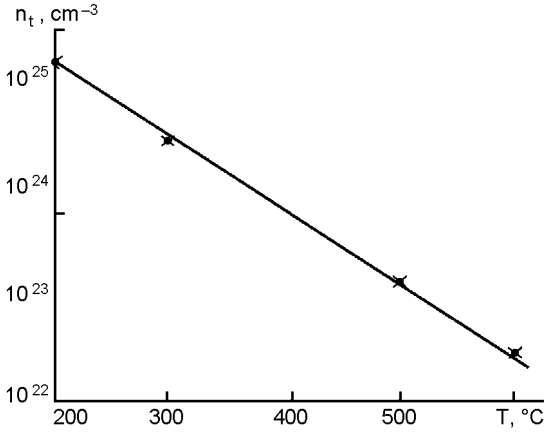

Fig. 4. Concentration of defects influencing the GaP fundamental absorption as a function of annealing temperature.

In our case, $n_t = n_{0t}\exp(-A\,T)$. Then,

$$f(n_t) = const_2\exp\left(\frac{E_A}{kT}\right)\exp(-A\,T). \quad (15)$$

The reaction order is a complex temperature function. This means that there is no unique annealing mechanism till 600°C. The beginning of the $\alpha(h\nu)$ restoring might be the only exception: isothermal annealing of the electroconductivity at 130°C and 145°C allows to determine its activation energy $E_{activ.} = 1.5$ eV inherent in the point defect annealing. At higher temperatures, the restoring of irradiated crystal parameters could not be confined to diffusion processes only. The decay of disorder region complex defects as well as appearing of qualitatively new defects related to interacting primary defects, changes of their configuration and formation of high temperature complexes with impurities, etc., become critical. The set of the mechanisms mentioned causes the complex $f(n_t)$ dependence which defines the annealing reaction order.

4. Conclusions

It has been stated that fast particle irradiation of GaP crystals causes the distortion of the fundamental absorption edge: the $\alpha(h\nu)$ curve slope changes and the main absorption band shifts to the region of lower quantum energy. The dependence of the absorption coefficient as a function of concentration of radiation defects which influence the optical transmission is exponential. The change of the $\alpha(h\nu)$ curve slope in the near-edge region with the fluence is described by the Urbach law and is interpreted as an increase of the TSD amplitude and density.

The shift of the absorption edge is caused by the Franz-Keldysh effect due to the inner fields of radiation defects. The effect increases the probability of the carrier tunneling involving a photon. The irradiated sample transmission is not restored fiully even at $T = 600$°C and is characterized by a variety of the annealing mechanisms. The function which defines the defect reaction order depends on temperature. Simple point defects are annealed at the initial heating stages before 200°C with activation energy equal to 1.5 eV.

References

1. E.Ju.Brailovskij, N.E.Yrigorian, Y.Eritzian, *Phys. Stat. Sol. A*, **62**, 649 (1980).
2. T.Endo, Y.Nakanishi, T.Wada, *Jap. J. Appl. Phys.*, **21**, 1619 (1982).
3. E.Yu.Brailovskii, N.I.Ostashko, V.P.Tartachnyk, V.I.Shakhovtsov, *Ukr. Fiz. Zh.*, **26**, 973 (1981).
4. A.P.Kudin, V.S.Manzhara, V.P.Tartachnyk, *Ukr. Fiz. Zh.*, **30**, 986 (1985).
5. D.B.Goer, A.A.Kolb, A.N.Krupkin, *Ukr. Fiz. Zh.*, **34**, 682 (1989).
6. M.Palezewska, J.Jasinski, K.Korona, M.Kaminska, *J. Appl. Phys.*, **78**, 3680 (1995).
7. V.M.Andreev, L.M.Dolginov, D.N.Tretykov. Liquid Epitaxy in Semiconductor Device Technology, Sov. Radio, Moscow (1975) [in Russian].
8. R.D.Sudlow, A.Mottram, A.R.Peaker, *J. Mater. Sci.*, **7**, 168 (1975).
9. J.Pankov, Optical Processes in Semiconductors, Prentice, New-York, 1971(Mir, Moscow 1973 in Russian).
10. V.A.Bonch-Bruevich, I.P.Zvyagin, R.Kaiper, A.G.Mironov, Electron Theory of Disordered Semiconductors, Nauka, Moscow (1981) [in Russian].
11. V.Opilat, P.Litovchenko, V.Kuts, V.Tartachnyk, *Ukr. Fiz. Zh.*, **36**, 776 (1991).
12. G.J.Dienes, G.H.Vineyard, Radiatiuon Defects in Solids, Interscience Publ., New-York (1957); Inostr. Liter., Moscow (1960) [in Russian].

Особливості білякрайового оптичного поглинання опроміненого GaP:Te

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Досліджено вплив проникаючої радіації на монокристали GaP:Te. Показано, що опромінення електронами $E = 50$ МеВ призводить до поступової деградації краю поглинання за рахунок невертикальних переходів між хвостами зон. Відпал радіаційних дефектів у зразках GaP, опромінених нейтронами реактора ($\Phi = 3 \cdot 10^{16}$ н/см^2), навіть при $T_{відп.} = 600$°C не спричиняє повного відновлення їхніх параметрів. Подальше підвищення температури кристала може привести до виникнення в ньому термодефектів, котрі різко погіршують однорідність зразка.